First Principles Calculations of Existing and Novel Electrode Materials

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Overview

Timeline

- Start Date Oct 1 2016
- End Date: Sept 2020

Budget

- Total budget (4 years): $1,800K
- FY16 funding $450

Barriers Addressed

- Low rate capabilities
- high cost
- poor stability
- low energy-density
- Poor understanding of oxygen redox

Partners/Collaborations within the VT program

- **Kristin Persson** (LBNL), **Mahalingam Subramanian** (ANL), **Dong Su** (BNL), **Feng Wang** (BNL), **NCEM** (LBNL), **G. Chen** (LBNL), **Brian McCloskey** (UC Berkeley)

Relevance

Relevance

- **Capacity** improvements on stoichiometric layered materials such as LCO, NMC, NCA are becoming limited
- **Li-excess** materials and **cation-disordered** materials have shown promise for significantly higher capacity and allow for a broad compositional range, but the physical mechanisms that control their redox behavior, mobility, capacity and stability, are poorly understood.

Objectives

- To understand the role of Li-excess in making high capacity, high energy density cathode materials
- To understand how Li-excess and cation disorder influence participation of oxygen ions in the redox activity.
- To use the concepts of cation disorder and oxygen redox to create high capacity cathodes
- Compare and contrast Na-ion and Li-ion layered intercalation cathodes and explore opportunities for Na cathodes.

Milestones

Month Year	Milestone	Status
Dec 2016	Computational approach to predict cation disorder and synthesis temperature	Complete
March 2017	Comparison of electronic structure modeling with experimental spectra	Complete
June 2017	Use modeling to come up with a new cation-disordered material	On track
Sept 2016	Demonstrate reduced surface oxygen loss by surface modification of a disordered cathode material using DEMS or TEM	On track – ahead of schedule

Approach

Use first principles computations and selected experiments to understand and design materials

Approach

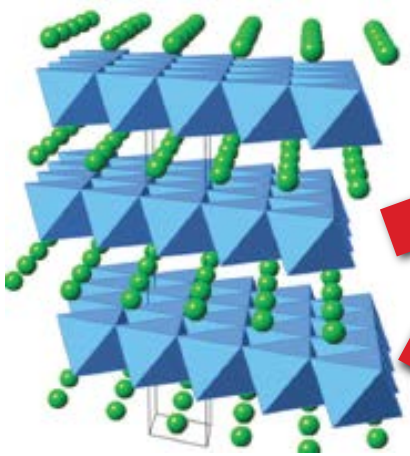
- Layered cathode materials are best bet for high energy density, but seem to be practically limited to ≈ 200mAh/g. How can we achieve theoretical capacity (280 mAh/g) ?
- Cation-disordered materials have more regularly changing lattice parameters and Li-ion mobility as function of state of charge,
- To broaden compositional space of cathodes, need to understand effect of cation disorder
- Li-excess and cation disorder both make oxygen redox easier. Need accurate approach to predict oxygen redox and its consequences

Methods

- DFT in GGA and GGA+U are used as implemented in VASP software
- Calibrated accurate HSE method on know spectral data so that competition between oxygen and transition metal redox can be computed
- Activation energies for Li/Na transport obtained from Nudged Elastic Band Calculations or Transition State assumptions
- Percolation theory (implemented with Monte Carlo) used to understand diffusion on macroscopic scale

Novel Directions for Cathodes

Stoichiometric layered



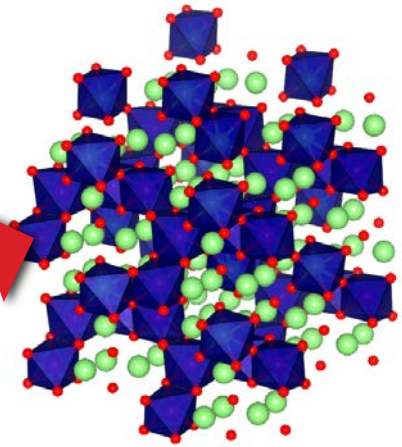
$LiCoO_2$

$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$

$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$

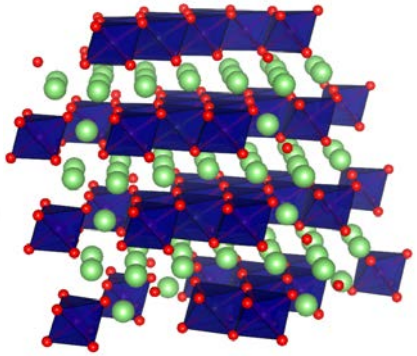
Only Co,Ni and Mn; Chemistry choices are fully exploited

Li-excess + disorder



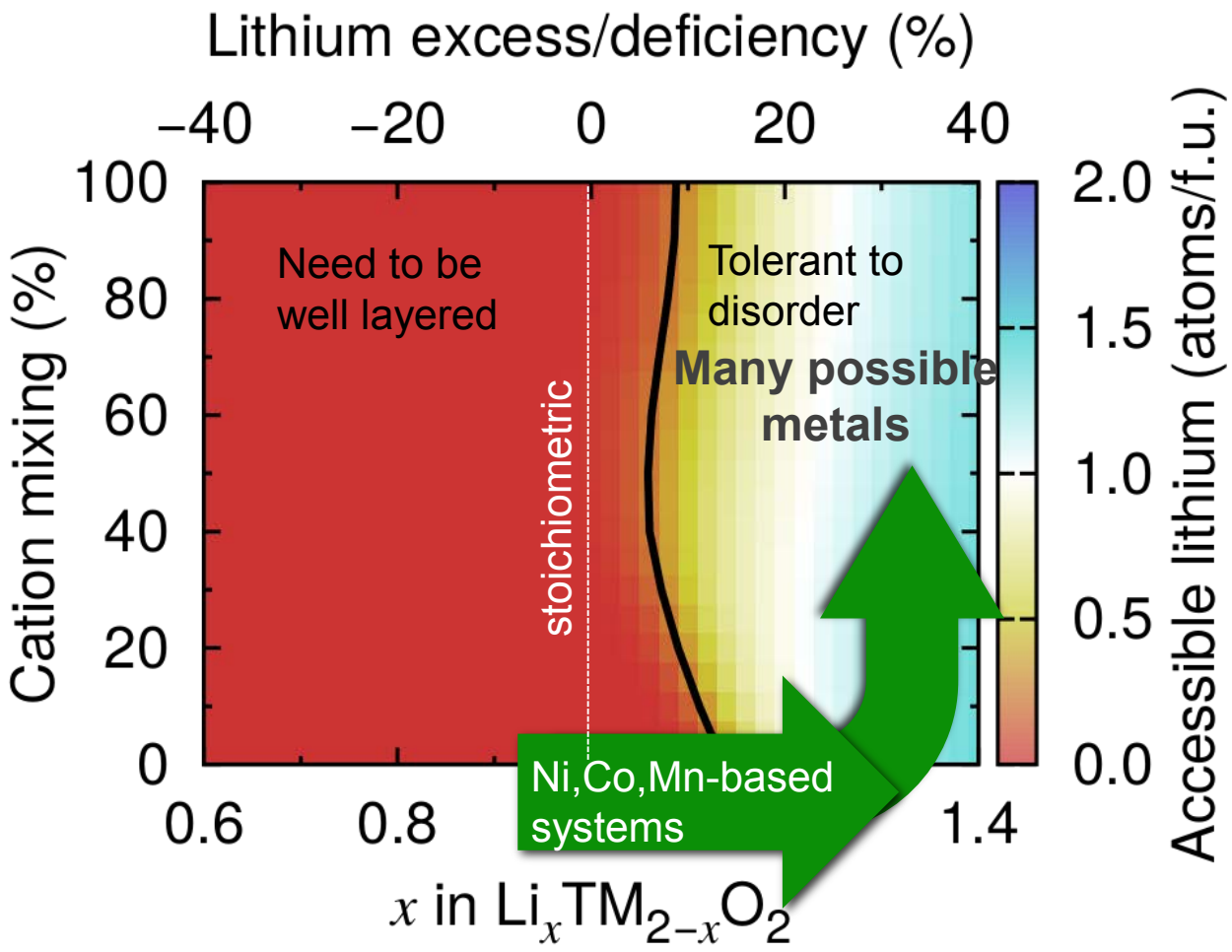
$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$
$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$
$Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$
Li_2VO_2F
$Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$
$Li_{(1+x)}Ti_{2x}Fe_{(1-3x)}O_2$

Layered Li-excess



LRNMC
$Li_2Ru_{0.75}Sn_{0.25}O_3$
Li_2IrO_3

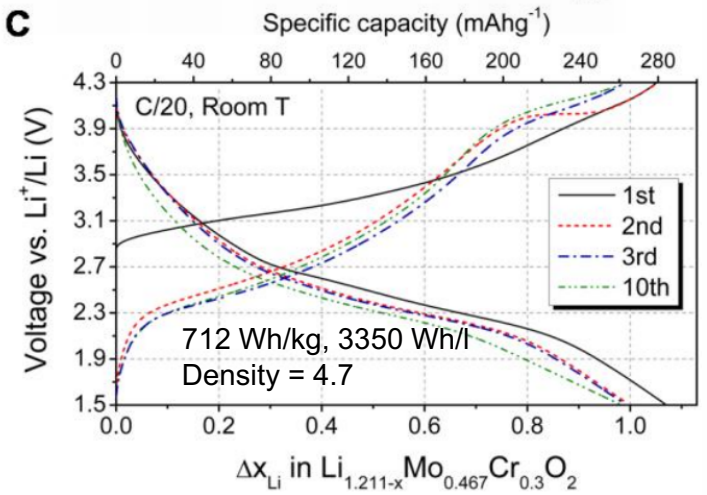
Disordered Cathodes Function only with Li-excess



Design Criteria: Need Li-excess > 10% to enable cation-disordered cathodes

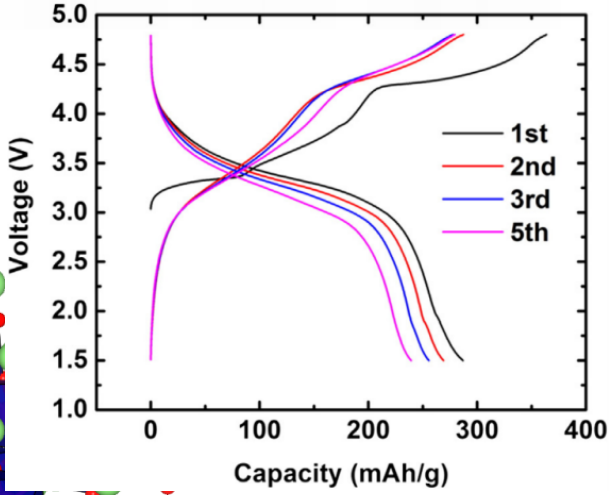
Now also lots of Li-excess disordered materials

$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$

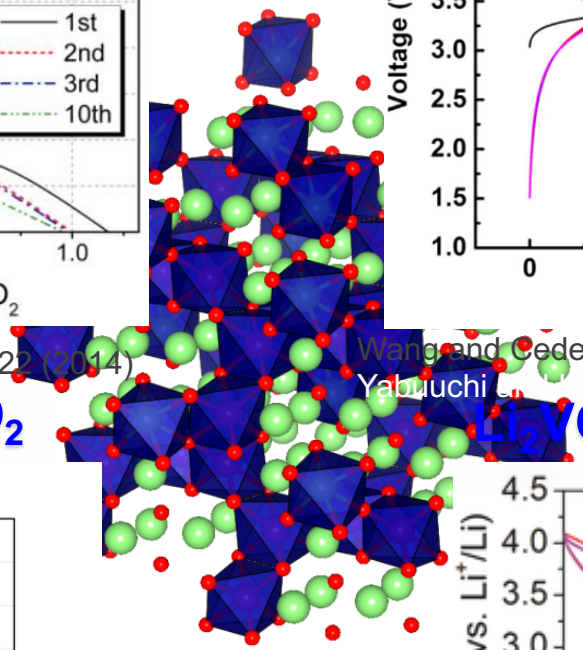


J. Lee, et al. Science, 343 (6170), 519-522 (2014)

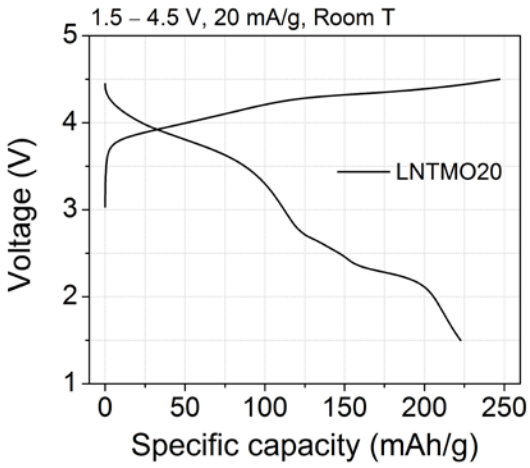
$Li_{1.25}Nb_{0.25}Mn_{0.5}O_2$



Wang and Ceder , Electrochem Comm. V**60** P 70-73 2015

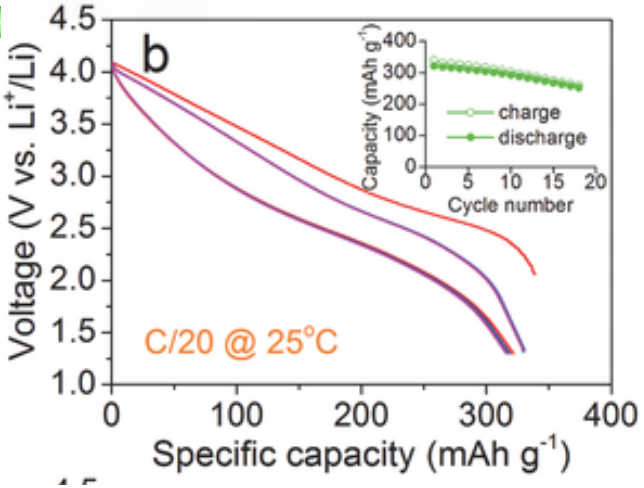


$Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$



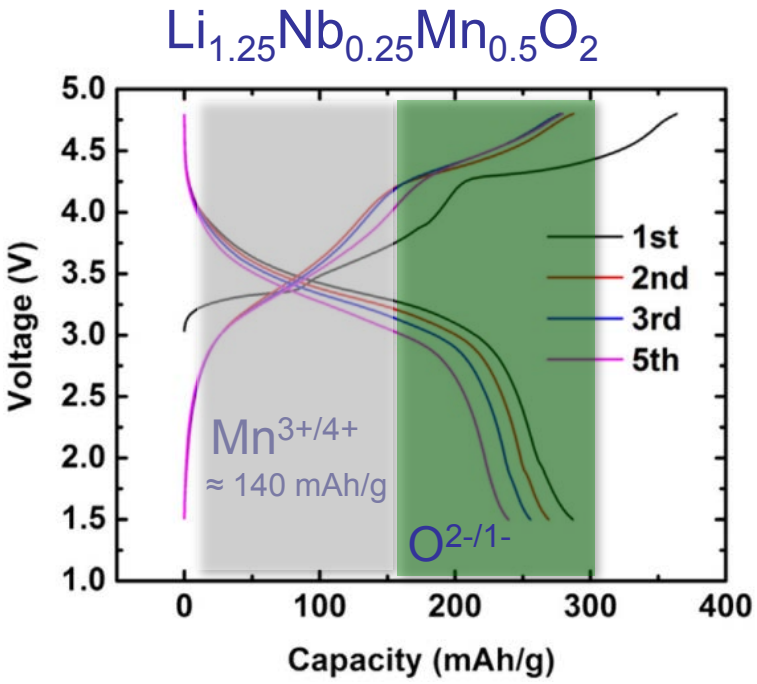
J. Lee and G. Ceder, Energy Environ. Sci., 8 (11), 3255-3265 (2015).

Li_2VO_2F



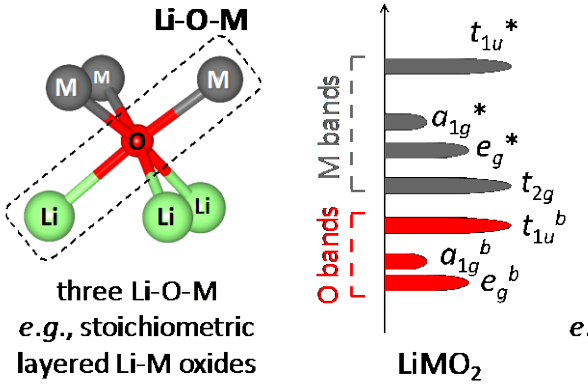
Chen R.,Fichtner Adv. Energy Mater., 5: 1401814. 2014

Technical Accomplishments (2): Reversible Oxygen Redox

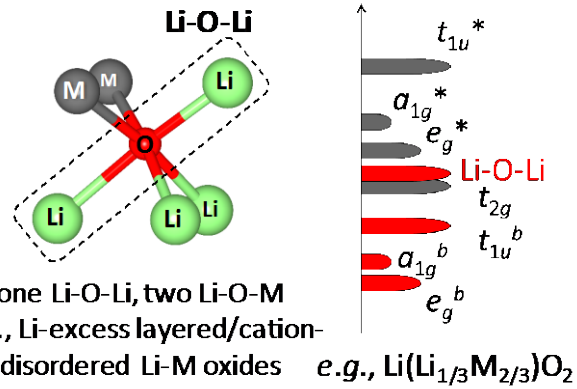


1) EELS confirms that about half of the capacity is reversible oxygen oxidation
2) We understand that oxygen anions become susceptible to oxidation when they are surrounded by Li on both sides

Layered environment:
no oxidation



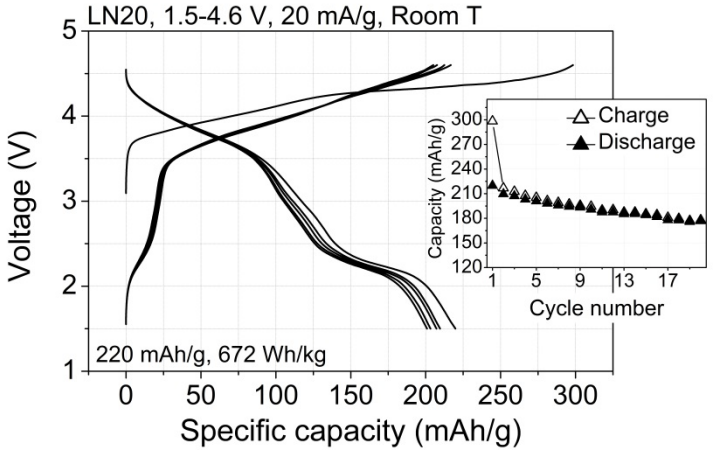
Li-excess environment:
oxidation

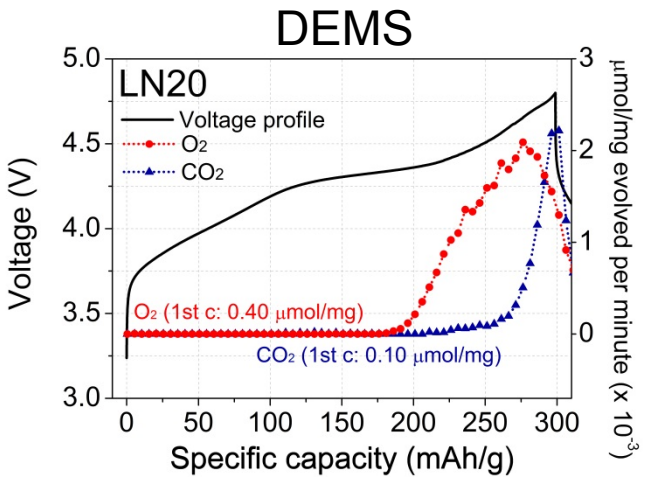


Nature Chem., (2016)

Technical Accomplishments: Stabilize LNTO

Last year: $Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$

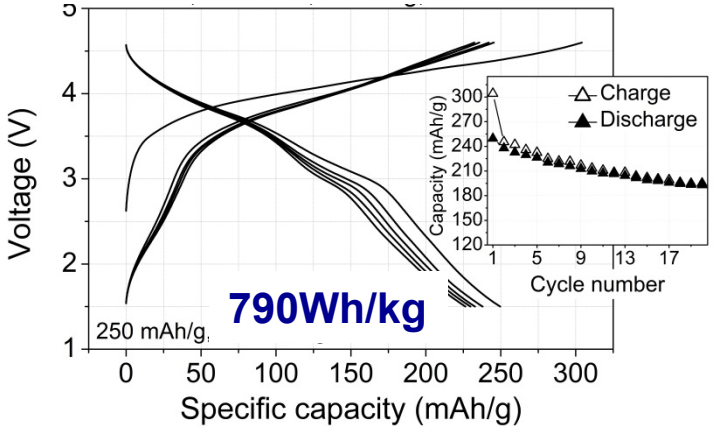


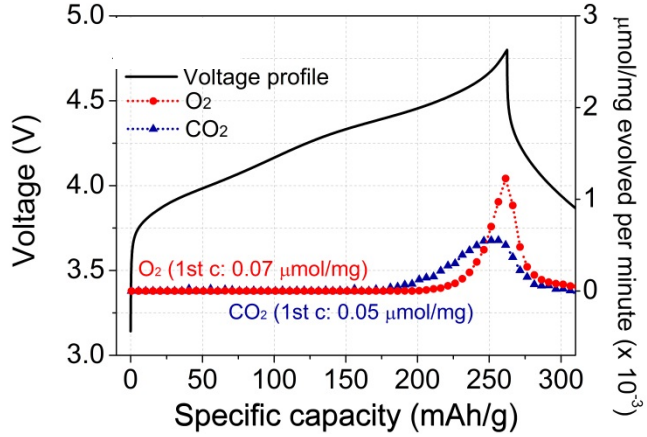


Good performance, but oxygen loss leads to polarization build-up

DEMS shows O-loss

Compositionally modified LNTO





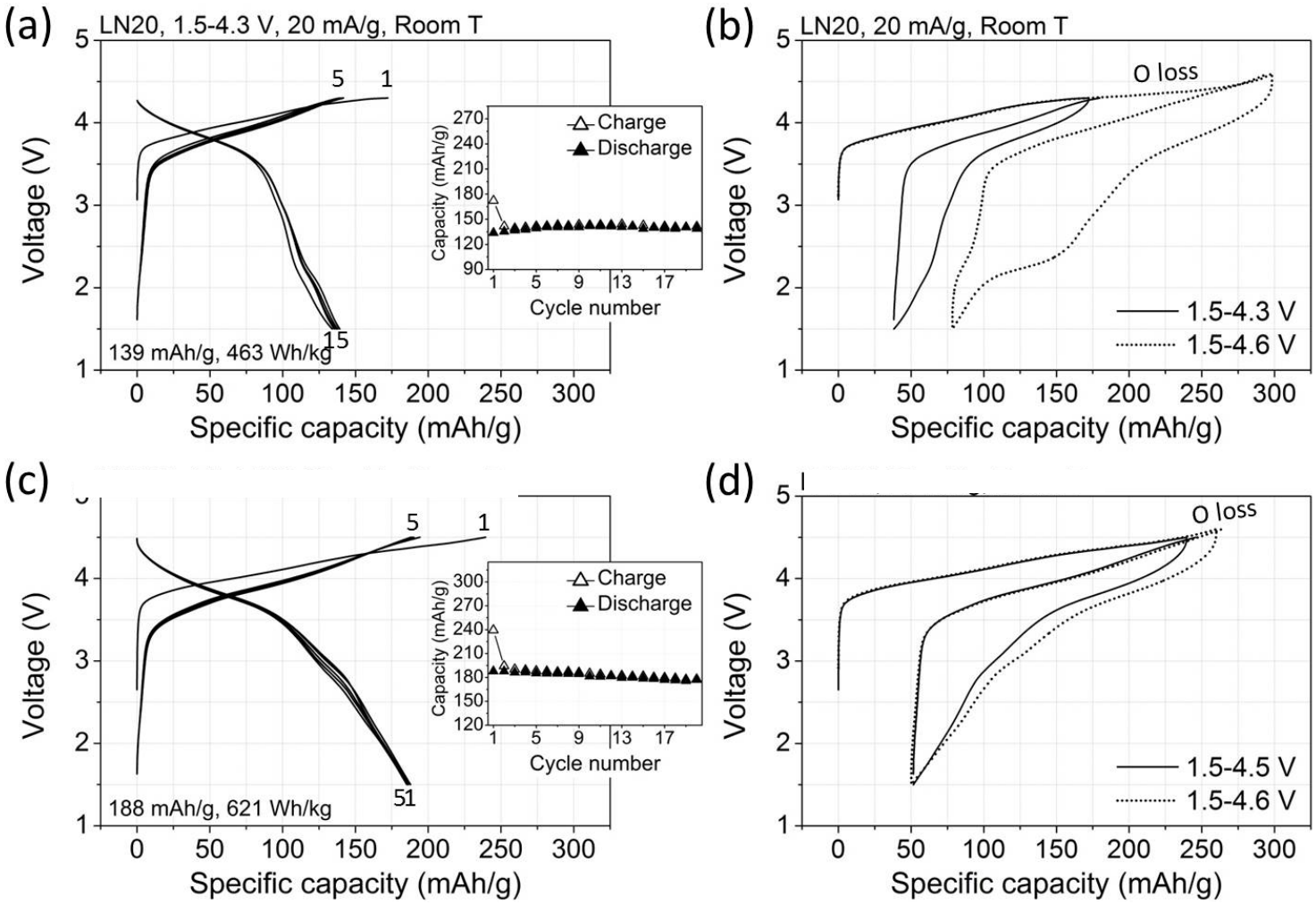
Less polarization and less O-loss

Submitted: Collaboration with Bryan McCloskey

Peer Review, Washington June 2017

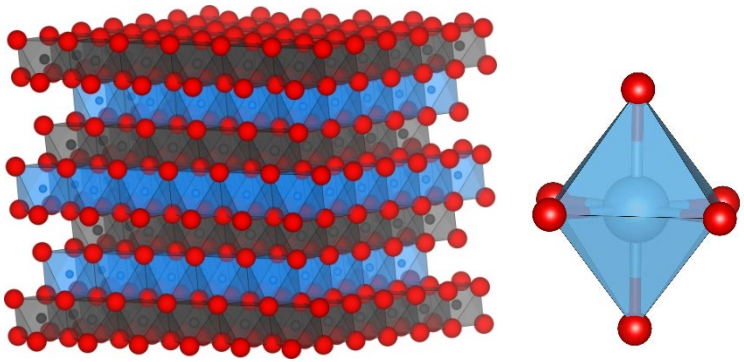
Stabilization leads to reduced polarization

Modified and unmodified $Li_{1.2}Ni_{0.32}Ti_{0.35}Mo_{0.135}O_2$

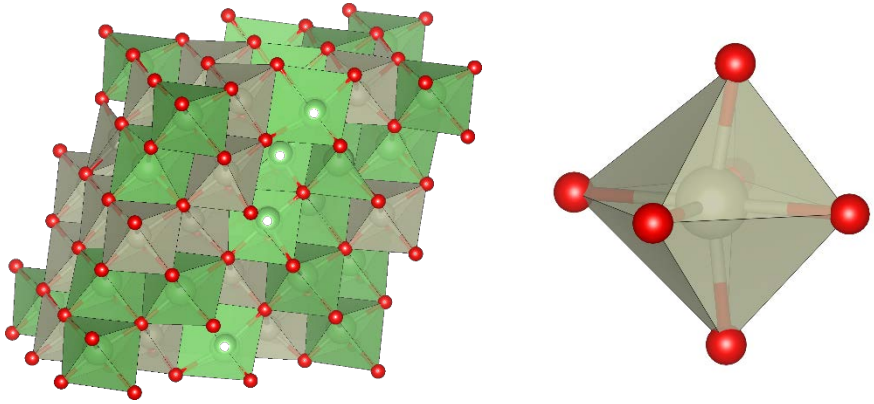


Understanding what drives disorder: d^0

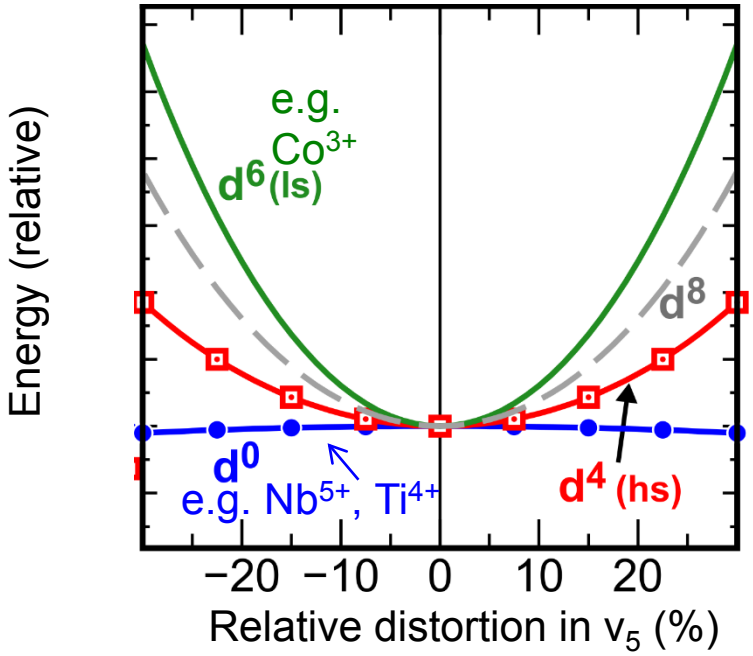
Layered



Cation Disordered



Ability to accommodate distortions depends on electronic structure



d^0 TMs are not sensitive wrt. site distortions

Layered compounds have fairly regular octahedral environments. Cation-disordered compounds have a range of distorted environments

d^0 TMs Accommodate Distortions and Promote Cation Disorder

50 most stable configurations (out of ~500)

$LiNi_{0.5}Ti_{0.5}O_2$

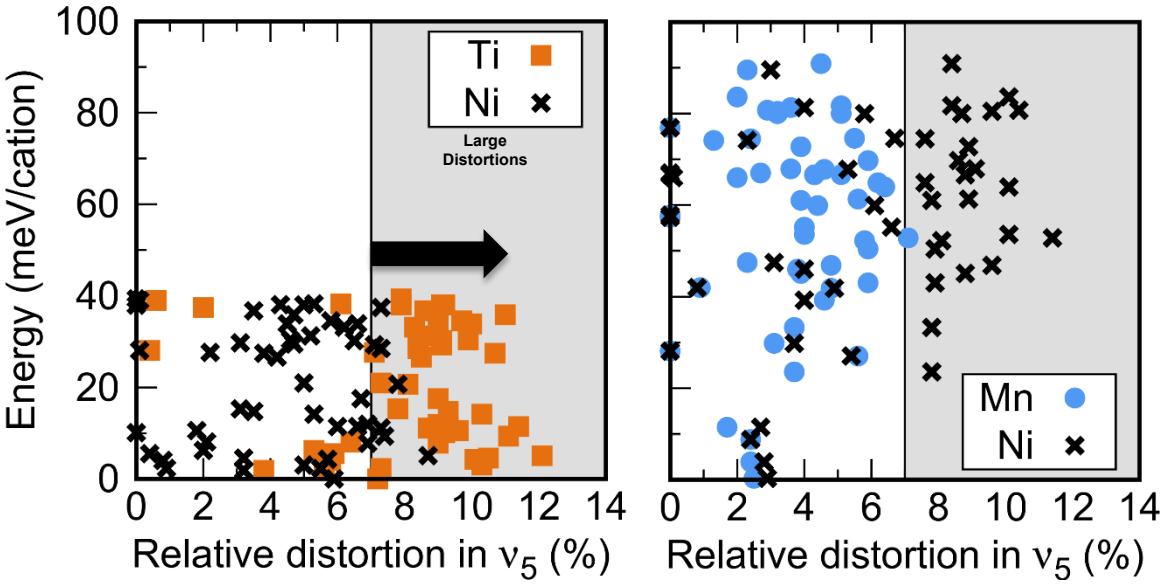
d^0 Ti^{4+} absorbs distortions

→ Ni^{2+} sites close to ideal

$LiNi_{0.5}Mn_{0.5}O_2$

d^8 Ni^{2+} distorts strongly

→ Steep energy increase



d^0 elements such as Ti^{4+}, Mo^{6+}, V^{5+}, Nb^{5+},Zr^{4+} easily accommodate distortions and thereby help stabilize disorder

Published Cation-Disordered $LiMO_2$ Compositions

Contain d^0 Transition-Metal Species

Composition	TM Cations
$Li_{1+x}V_2O_5$	V^{3+}, **V^{5+}**
$LiM_{0.5}Ti_{0.5}O_2$ (M = Fe, Ni)	M^{2+}, **Ti^{4+}**
$Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$	Mo^{5+}, Cr^{3+}
$Li_{1.3}Nb_{0.3+x}M_{0.4-x}O_2$ (M = Mn, Fe, Co, Ni)	**Nb^{5+}**, M^{3+}
$Li_{1.6-4x}Mo_{0.4-x}Ni_{5x}O_2$	**Mo^{6+}**, Ni^{2+}
$Li_{1.3}Nb_{0.3}V_{0.4}O_2$	**Nb^{5+}**, V^{3+}
$LiCo_{0.5}Zr_{0.5}O_2$	Co^{2+}, **Zr^{4+}**

Disorders when Mo^{5+} is oxidized to d^0 Mo^{6+}

C. Delmas, S. Brèthes, and M. Ménétrier, *J. Power Sources* **34**, 113 (1991).
L. Zhang, H. Noguchi, D. Li, T. Muta, X. Wang, M. Yoshio, and I. Taniguchi, *J. Power Sources* **185**, 534–541 (2008).
H. Shigemura, M. Tabuchi, H. Sakaebe, H. Kobayashi, and H. Kageyama, *J. Electrochem. Soc.* **150**, A638 (2003).
J. Lee, A. Urban, X. Li, D. Su, G. Hautier, and G. Ceder, *Science* **343**, 519 (2014).
R. Wang, X. Li, L. Liu, J. Lee, D.-H. Seo, S.-H. Bo, A. Urban, and G. Ceder, *Electrochem. Commun.* **60**, 70–73 (2015).
N. Yabuuchi, S. Komaba *et al.*, *Proc. Natl. Acad. Sci. USA* **112**, 7650–7655 (2015).
N. Yabuuchi, Y. Tahara, S. Komaba, S. Kitada, and Y. Kajiya, *Chem. Mater.* **28**, 416 (2016).
N. Yabuuchi, M. Takeuchi, S. Komaba, S. Ichikawa, T. Ozaki, and T. Inamasu, *Chem. Commun.* **52**, 2051 (2016).
A. Urban, I. Matts, A. Abdellahi, and G. Ceder, *Adv. Energy Mater.* **6**, 1600488 (2016).

Remaining Challenges and Barriers

- While reversible bulk oxygen redox is now confirmed, and its structural/chemical origin understood from theory, it is important to better understand whether or not it enhances surface reactivity with the electrolyte. Combined modeling/TEM studies will be performed to look at the surface of cycled cathode materials with oxygen redox
- Rate capability of disordered materials needs to be improved further, but maybe an issue of surface transformations (as in other high capacity layered materials).

Proposed Future Work

- Further confirm under which conditions reversible bulk oxygen redox activity takes place (e.g. which voltage, chemistry, structural features): Collaboration ongoing with ALS to correlate oxygen K-edge with theory results. Collaboration with National Center for Electron Microscopy (NCEM - LBNL) for advanced EELS on anion-active materials
- Modeling + TEM of surface transformations that occur in cathode materials to better understand oxygen loss at cathode surface
- Further test and characterize compositional modifications to reduce oxygen loss and reduce polarization build-up
- New disordered compositions with specific energies approaching 1000Wh/kg

New Project: Protecting Li-metal

Project just started March 2017

1. Assessment of the chemical and electrochemical stabilities of the solid electrolytes.

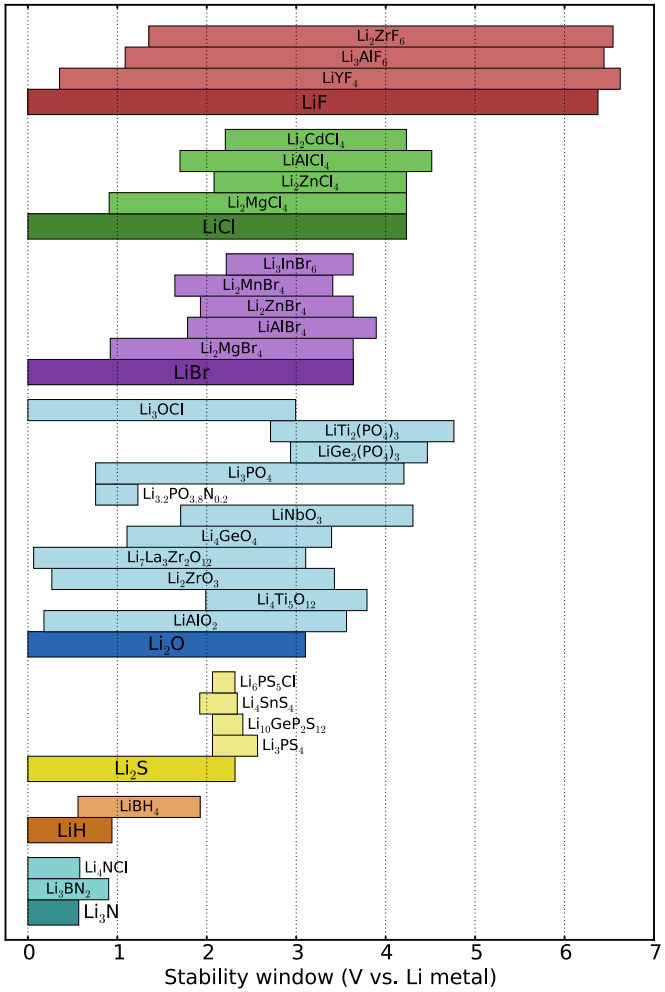
2. Li-metal coating layers.

3. Evaluation of the ionic conductivity of Li in promising solid electrolytes and interfacial products

4. Assess the resilience of solid electrolytes and interfacial products towards Li-dendrite growth and propagation using models developed to understand dendritic growth.

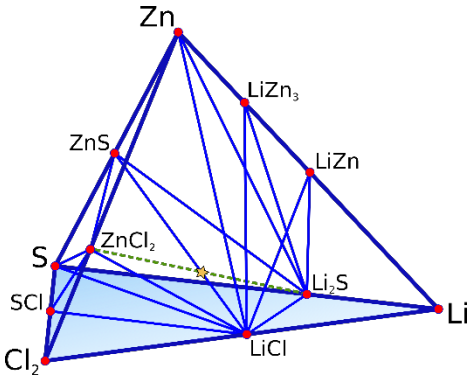
Approach

Modeling of voltage window of conductors



W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim, and **G. Ceder**, *Chem. Mater.* **28** (2015) 266-273.

Interfacial reactions between Li and conductors



For example predicted that LiPON will decompose to Li_3N at Li metal interface

Also developing models for dendrite growth (mechanical and chemical)

Summary

Li-excess disordered cathodes are an exciting new direction to develop high energy density cathodes. They broaden the chemical space in which one can design dense cathodes.

- Our percolation theory shows that once the Li excess content is > ≈ 10% rocksalt-like compounds such as layered materials become tolerant to cation disorder, even to the point where fully cation-disordered materials have large reversible capacity. This tolerance to disorder enables novel compositions as “well-layeredness” is not a requirement anymore.
- We have demonstrated the new percolation concepts on two new materials with capacity > 200 mAh/g (Nb-Mn and Ti-Ni-Mo based).
- We have demonstrated that reversible oxygen oxidation contributes substantially to the capacity of Li-excess and cation-disordered materials
- Carefully calibrated and novel first principles modeling has identified unbonded oxygen states, arising from linear Li-O-Li configurations in the cathode materials as the source of reversible oxygen redox.
- Compositional modification can reduce the first cycle oxygen loss and reduce the polarization
- We have shown through theory and modeling why d^0 elements leads to more disordered compounds.

Collaborations

Collaborations with Kristin Persson (LBNL), **Mahalingam Subramanian** (ANL), **Dong Su** (BNL), **Feng Wang** (BNL), **NCEM** (LBNL), **G. Chen** (LBNL), **Brian McCloskey** (UC Berkeley)